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## (54) PROCESS FOR REGENERATING USED POLYTETRAFLUOROETHYLENE

(71) We, INSTITUT KHMICHESKOI FIZIKI AKADEMII NAUK SSSR, a state enterprise organised and existing under the laws of the Union of Soviet Socialist Republics (U.S.S.R.), of 2b Vorobievske shosse, Moscow, U.S.S.R., do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

The present invention relates to the regeneration and modification of used polytetrafluoroethylene (PTFE).

The search for new processes for regeneration and modifying regeneration of polytetrafluoroethylene ( $-CF_2-CF_2-$ )<sub>n</sub> is encouraged by the fact that during use polytetrafluoroethylene is not susceptible to oxidation and ageing and therefore retains all the complex of valuable properties inherent in molecules of perfluorinated polymers; in addition, polytetrafluoroethylene is rather expensive. Amounts of used polytetrafluoroethylene available for regeneration are 65 to 85% of the annual production of PTFE. This is made up of residual material from scrap articles and also waste products arising from the thermal and mechanical processing of polytetrafluoroethylene blanks.

It is an object of the present invention to

provide a process for regeneration of used polytetrafluoroethylene.

According to the present invention we provide a process for reprocessing used polytetrafluoroethylene comprising providing said used polytetrafluoroethylene in the form of a powder composed of discrete particles of size not greater than 100 $\mu$ , irradiating said powder with ionising radiation to activate the polytetrafluoroethylene and contacting the activated polytetrafluoroethylene with a fluorinated monomer of formula  $C_2F_xR_{4-x}$  in which x is an integer from 1 to 4, R is hydrogen, a trifluoromethyl group, a chlorine atom, a phenyl group or a pentafluorophenyl group, thereby effecting copolymerisation of the polytetrafluoroethylene with the said monomer.

The polytetrafluoroethylene powder may be suspended in water or in one of the said fluorinated monomers and irradiated in the suspended state.

The activation is preferably effected under an atmosphere containing not more than  $2 \times 10^{-3}$  vol % of oxygen, said atmosphere being provided by carrying out the activation (a) under a reduced pressure of inert gas or fluorinated monomer vapour not lower than 5 mm Hg, or, (b) under reduced pressure not exceeding  $1 \times 10^{-2}$  mm Hg, or (c) under pressure of the vapour of said monomer of

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- from 0.1 to 50 atmospheres.
- It is advisable to use, in accordance with the present invention, gamma-radiation as the ionizing radiation, or X-rays, beta-radiation or accelerated electrons.
- When the used polytetrafluoroethylene is employed in the form of a dry powder, it is advisable, in accordance with the present invention, to effect the activation by means of a plasma treatment.
- The term "plasma treatment" means the treatment of the used polytetrafluoroethylene powder with an electronic and ionic plasma which is formed in the zone of a high-frequency discharge in an atmosphere of inert gases such as helium, neon, argon or in an atmosphere of a monomer, i.e. tetrafluoroethylene under a pressure of down to 5 mm Hg. Under the action of the plasma electrons and ions having an energy of from 10 to 30,000 ev, on the surface of a used PTFE powder there are accumulated free radicals in a concentration of up to  $10^{18}$  radicals/g of the used PTFE being treated which is equivalent to an integral dose of about  $5 \times 10^5$  Rad.
- The process for regenerating used polytetrafluoroethylene according to the present invention has two principally different embodiments, i.e. with the formation of a pure regenerate and of a modified regenerate.
- By the term "pure regenerate" is meant a regenerate produced as a result of a radiation-graft block copolymerization of a used polytetrafluoroethylene with its own monomer, viz. tetrafluoroethylene.
- By the term "modified regenerate" is meant a regenerate produced as a result of a radiation-graft block copolymerization of a used polytetrafluoroethylene with a monomer of the formula  $C_2F_xR_{4-x}$  where  $x = 1$  to 3 at  $R=H$ ;  $x = 3$  at  $R=CF_3, C_1, C_6H_5, C_6F_5$ . Said monomers include (a) compounds capable of formation, under the conditions of the process of the present invention, of grafted block copolymers with a used polytetrafluoroethylene thus imparting novel properties thereto, and (b) compounds, referred to hereinafter as "inactive monomers", which cannot, per se, take part in the reaction of graft block copolymerization with a used polytetrafluoroethylene and are employed only in the form of mixtures with said reactive fluorinated monomers. The reactive monomers, in addition to tetrafluoroethylene, may be exemplified by trifluorochloroethylene, trifluoroethylene and the like.
- The inactive monomers may be exemplified by fluorinated compounds of the formula:  $C_2F_xR_{4-x}$  where  $R$  is  $CF_3, C_6F_5, C_6H_5$  at  $x=3$ , or ethylene or vinyl chloride.
- In the case of a pure regeneration where as the fluorinated monomer use is made of tetrafluoroethylene, the block copolymerization in accordance with the present invention should be preferably performed in an aqueous suspension of a used polytetrafluoroethylene powder with a mean particle size of at most  $30\mu$ ; said suspension is activated in an atmosphere of tetrafluoroethylene with a total dose of from  $1 \times 10^3$  to  $1 \times 10^4$  Rad, at a dose rate of from  $1 \times 10^{-2}$  to 10 Rad/sec at the temperature of  $70^\circ C$  under a pressure of tetrafluoroethylene of from 0.1 to 5 atm.
- In the case of a modified regeneration where as the fluorinated monomers use is made of the compounds of the formula  $C_2F_xR_{4-x}$  where  $x=1$  to 3 at  $R=H$ ;  $x = 3$  at  $R = Cl$ , it is advisable, according to the present invention, to effect activation of the polytetrafluoroethylene suspension in an atmosphere of at least one of said fluorinated monomers with a total dose of from  $1 \times 10^3$  to  $1 \times 10^5$  Rad, dose rate of from  $1 \times 10^{-1}$  to 50 Rad/sec and at a temperature of from  $-20$  to  $100^\circ C$ .
- The dose rate is further increased when a modified regeneration is effected with the use of said inactive fluorinated or chlorinated monomers. Thus, according to the present invention, in the case of using a mixture of a fluorinated monomer of the formula  $C_2F_xR_{4-x}$  where  $x = 1$  to 4 at  $R=H$  and  $x=3$  at  $R=Cl$ , with ethylene, vinyl chloride or a compound of the formula  $C_2F_xR_{4-x}$  where  $x=3$  at  $R=CF_3, C_6H_5, C_6F_5$ ; activation of the used polytetrafluoroethylene suspension is effected in the atmosphere of said mixture of the monomers with a total dose of from  $1 \times 10^4$  to  $1 \times 10^6$  Rad, at a dose rate of from 1 to  $10^2$  Rad/sec, at a temperature within the range of from 30 to  $100^\circ C$  and under a pressure of said monomer mixture of from 1 to 50 atm.
- The total dose of the ionizing radiation may be decreased in the case if, according to the present invention, the used polytetrafluoroethylene powder is first irradiated at a temperature of from  $-196$  to  $-130^\circ C$  under a reduced pressure of not more than  $1 \times 10^{-2}$  mm Hg, whereafter at least one of active fluorinated monomers of the formula  $C_2F_xR_{4-x}$  where  $x$  is an integer from 1 to 4,  $R$  is hydrogen or  $x$  is 3 and  $R$  is chlorine is added, the temperature is raised to  $0^\circ C$ ; water is added to form an aqueous suspension of the activated polytetrafluoroethylene and the graft block-copolymerization is completed at a temperature of from 0 to  $100^\circ C$ .
- A distinctive feature of the process for regenerating a used polytetrafluoroethylene according to the present invention resides in the fact that the object of the invention is accomplished with only a small consumption rate of the fluorinated monomers, namely of from 5 to 50% by weight of the used PTFE being regenerated.
- As is seen from the foregoing, the process of the present invention makes it possible to produce, on the basis of used polytetrafluoroethylene, a novel class of graft block copolymers having a commercial interest. Furthermore, the process of the present

invention makes it possible to use, in addition to active fluorinated monomers capable of taking part in the reaction of homopolymerisation under radiation activation conditions, also inactive fluorinated and non-fluorinated monomers which do not take part in the homopolymerisation reaction under said conditions ( $C_2F_3CF_3$ ,  $C_6F_5C_2F_3$ ,  $C_2H_3Cl$ ,  $C_6H_5C_2F_3$ ,  $C_2H_4$ ).

Regeneration according to the process of the present invention is applicable to a used polytetrafluoroethylene available from practically all sources thereof—from the residual material of spent articles and production wastes of thermal and mechanical processing of article blanks consisting of a pure of composite polytetrafluoroethylene.

The process for regenerating used PTFE according to the present invention consists in the steps of preparation and purification of the raw material, crushing, finely dividing, fractionation and a pure radiation graft regeneration or a modified regeneration with subsequent processing of the regenerates into articles. Prior to crushing, used PTFE should be subjected to purification from foreign matter and oils inhibiting graft block copolymerization. Application of different purification methods depends on the degree of contamination of used PTFE to be regenerated. Special care should be taken during the purification step in order to obtain regenerates with good physico-mechanical, electrical and other properties. Dust elimination is effected by flotation, dissolving dust in acids or mechanical removal of a thin contaminated layer from large articles. Oil removal is effected by way of a treatment of chips and lumps of used PTFE with organic solvents extractants. A preferable embodiment of the starting material purification from organic substances and dust consists in a heat treatment of the material prior to crushing at a temperature of from 300 to 360°C for 1-2 hours with an arbitrary rate of the temperature raise. Cooling conditions may be optional as well or they may be controlled for the purpose of producing a required crystallinity degree. Purified used PTFE is then fed to mechanical crushing and fine grinding.

One of the basic conditions for effecting the process of the present invention resides in the production of a finely divided powder of a used polytetrafluoroethylene with a particle size of at most 100 $\mu$ ; in the case of a pure regeneration where as the fluorinated monomer use is made of tetrafluoroethylene a mean particle size of the used polytetrafluoroethylene powder should not exceed 30 $\mu$ . Moreover, the used PTFE powder should comprise a rather narrow fraction with a fineness not exceeding a mean particle size of the PTFE powder. Therewith, the greater the specific surface area of the powder, the better the quality of a regenerate.

Powdered used PTFE with a particle size of not more than 100 $\mu$  and with a mean particle

size of from 10 to 30 $\mu$  can be obtained, for example, by using a plant for low-temperature crushing and fine grinding.

In said plants used polytetrafluoroethylene and grinding mechanisms are cooled by liquid nitrogen at a temperature below the glass transition temperature of polytetrafluoroethylene, i.e. below -130°C and down to -196°C. As the grinding mechanisms use is made of knife crushers, disintegrating mills, vibromills or jet-mills.

A low-temperature scheme of disintegration of used polytetrafluoroethylene makes it possible to minimize contamination of PTFE as well as transfer of the material of working members to the PTFE being disintegrated.

Regeneration of used PTFE is effected in a radiation chemical reactor. Therewith, the following embodiments of the regeneration process are possible.

A suspension is prepared from a finely divided PTFE powder with a solids concentration of about 5 to 25% by weight. As the liquid phase of the suspension use may be made of both water and one of fluorinated monomers such as perfluorostyrene,  $\alpha$ ,  $\beta$ ,  $\beta$ -trifluorostyrene or trifluorochloroethylene. The liquid phase ensures the removal of heat evolving during the reaction of graft block copolymerization, prevents the powder surface from local over-heating and contributes to a more uniform grafting of a fresh polymer (copolymer) layer within the entire volume of the solid phase. Uniform distribution of the powder particles within the liquid phase is ensured by vigorous stirring. To stabilize the aqueous suspension, use is made of perfluorocarboxylic acids with 3 to 5 carbon atoms as stabilisers.

For a successful implementation of modified and, especially, pure regeneration processes it is important to select conditions ensuring a minimal dose of irradiation of used PTFE for a given yield of the graft block copolymer. The most preferred embodiment of the process according to the present invention resides in activation of the graft block copolymerization by way of irradiation of an aqueous suspension of used PTFE powder in the presence of tetrafluoroethylene or other fluorinated monomers or mixtures thereof.

This makes it possible to employ unstable radicals with a short life time as centres in the PTFE powder to be irradiated for the progress of the reaction. Their concentration is higher by more than an order of magnitude than the concentration of stable radicals.

Uniform distribution of bubbles of the gaseous phase of the fluorinated monomers in the aqueous suspension is ensured by vigorous stirring. Such process conditions are necessary to retain the process control, prevent the reaction from auto-acceleration and ensure a greater surface contact area of the gaseous phase of fluorinated monomers with the

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5 powder particles. The latter condition is of great importance, since the graft block copolymerization plays a greater role where there is an intimate contact between the powder and gaseous phase of the fluorinated monomers.

10 In all the embodiments of the process, to avoid excessive destruction of used PTFE catalysed by oxygen and to retain the process controllability, oxygen content should preferably not exceed its tolerable concentrations in the monomers. The practical purposes all the recommended fluorinated monomers have inherently an oxygen content which does not exceed  $2 \times 10^{-3}$  vol.%. The same low oxygen condition is preferred in the embodiment which specifies pre-activation of a powder by irradiation or plasma treatment under a residual pressure of the fluorinated monomers of  $1 \times 10^{-2}$  mm Hg.

15 Most advantageous for the performance of the process for regeneration of used PTFE in the presence of fluorinated monomers according to the present invention is the use of commercial sources of gamma-radiation. In the embodiment with a pre-activation of the surface of a dry powder of a used PTFE it is most preferable, for accumulation of stabilized radicals, to use radiations with a high linear energy transmission, i.e. beta-radiation, accelerated electrons or plasma treatment. As a result a reduced total dose is required for of the powder irradiation, the bulk destruction of the starting used PTFE is prevented and the yield of the product is lowered. Prior to the surface activation, the powder should be cooled to a temperature below its glass transition temperature, i.e. down to  $-196^{\circ}\text{C}$ .

20 In the process of a pure regeneration, i.e. when use is made of the most active monomer-tetrafluoroethylene, one can achieve a 50-100% conversion thereof in a grafted layer of the regenerate powder under rather mild conditions with a total dose of gamma-radiation from  $\text{Co}^{60}$  of from 1,000 to 3,000 Rad and, in any case, not more than 10,000 Rad.

25 In the embodiment of the process according to the present invention contemplating a pure regeneration there should be ensured for the purpose of increasing the ratio of yield of the grafted block copolymer to the homopolymer yield and increasing the fluorinated monomer pressure, a corresponding use of reduced dose rates within the above-said range. Generally, a graft block copolymerization starts right after the irradiations starts in the presence of a fluorinated monomer. As has been found in the control tests, homopolymerization of tetrafluoroethylene is preceded by an induction period which lasts from dozens of minutes to several hours. Duration of the induction period is increased at reduced dose rates. The homopolymer yield usually does not exceed 3

30 to 10% of the total conversion of tetrafluoro-

35 ethylene. Prior to the fluorinated monomer supply into a reactor and before the irradiation starts, a suspension of the PTFE powder is deaerated and freed from oxygen by way of passing high-purity nitrogen. To prepare the suspension, use is made of twice distilled water. For the pure regeneration process a temperature of about  $+70^{\circ}\text{C}$  is optimal, since it ensures a high rate of graft block copolymerization to be retained. A regenerated polytetrafluoroethylene prepared by the process of the present invention is washed with water and dried. It comprises a white bulky powder which may be processed by methods usually employed for a "fresh" polytetrafluoroethylene, i.e. compression moulding, sintering in a free state, extrusion and the like.

40 In the process of a modified regeneration, wherein use is made of other reactive fluorinated monomers such as  $\text{C}_2\text{F}_x\text{R}_{4-x}$  wherein  $x=1$  to 3 at  $\text{R}=\text{H}$  and  $x=3$  at  $\text{R}=\text{Cl}$ , mixtures thereof, mixtures of said fluorinated monomers with tetrafluoroethylene, as well as mixtures of said fluorinated monomers with less active fluorinated monomers such as  $\text{C}_3\text{F}_6$ ,  $\text{C}_2\text{F}_3\text{C}_6\text{H}_5$ ,  $\text{C}_2\text{F}_3\text{C}_6\text{F}_5$ , the activation should be performed, due to a reduced radiation-chemical yield of the graft block-copolymerization reaction, within a broader range of total doses, i.e. from  $1 \times 10^3$  to  $1 \times 10^5$  Rad. In such a case, for many of said fluorinated monomers and mixtures thereof such as  $\text{C}_2\text{F}_3\text{Cl}$ ,  $\text{C}_3\text{F}_8\text{H}$  or a mixture of  $\text{C}_2\text{F}_4$  and  $\text{C}_2\text{F}_3\text{Cl}$ , a total dose sufficient to obtain a graft block copolymer yield of from 20 to 50% by weight is close to the lower limit of said range and does not exceed 10,000 Rad. In the case of the modified regeneration in question the activation of the graft block-copolymerization reaction should

45 be preferably performed at a dose rate of from  $1 \times 10^{-1}$  to  $5 \times 10$  Rad/sec at a temperature ranging from  $-20^{\circ}\text{C}$  to  $100^{\circ}\text{C}$ . At temperatures above  $0^{\circ}\text{C}$  as a liquid phase use may be made of the fluorinated monomer employed such as trifluorochloroethylene. In each case an optimal temperature for the graft block copolymerization reaction is selected within the above-mentioned temperature range depending on the character of the fluorinated monomer or mixture of fluorinated monomers employed:  $-20$  to  $35^{\circ}\text{C}$  for  $\text{C}_2\text{F}_3\text{Cl}$ ;  $70^{\circ}\text{C}$  for  $\text{C}_2\text{F}_3\text{H}$ , etc. The above-mentioned group of fluorinated monomers under the above-described modified regeneration conditions is characterized by the absence of an induction period for the graft block-copolymerization reaction. The yield of a product in the absence of a reaction of a superficial radical chain transfer is also insignificant.

50 Still more severe conditions for the graft block-copolymerization reaction are necessary for a modified regeneration of a used polytetrafluoroethylene by means of mixtures of monomers containing, in addition to said reactive fluorinated monomers, also inactive or

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- less reactive monomers such as vinyl chloride and ethylene. In this case the activation is effected with higher total doses which may be as high as  $1 \times 10^4$  to  $1 \times 10^6$  Rad at a dose rate of 5 from 1 to  $10^2$  Rad/sec, under a total pressure of the mixture of said monomers ranging from 1 to 50 atm and at a temperature of up to 100°C.
- For all the disclosed embodiments of 10 regeneration of a used polytetrafluoroethylene by means of various groups of fluorinated monomers and mixtures thereof, the most preferred is the embodiment contemplating the use of an aqueous suspension of a used polytetrafluoroethylene powder.
- In the case where a dry powder of a used 15 polytetrafluoroethylene is subjected to activation, regeneration of said powder is effected using stabilized radicals, formed from the action, on the surface of said powder, of beta-radiation, accelerated electrons or plasma treatment. Stabilization of radicals on a dry powder of a used polytetrafluoroethylene is achieved by cooling it to a temperature below the glass transition temperature of polytetrafluoroethylene (about -130°C) and down to -196°C; for this purpose the powder is cooled, 20 prior to the activation, with liquid nitrogen. Such stabilized radicals are referred to as post-radicals.
- Accumulation of post-radicals is performed 25 at an integral dose ranging from  $1 \times 10^4$  to  $1 \times 10^6$  Rad in the presence or absence of fluorinated monomers. After the accumulation of said post-radicals, the temperature elevation (defrosting) must be effected in the presence of reactive fluorinated monomers which are condensed on to the powder prior to its activation or thereafter. Defrosting of the activated powder in the presence of fluorinated 30 monomers makes it possible to use, for the graft block copolymerization, the radicals formed within the temperature range of from -196° to 0°C, whereby the integral dose required to achieve a predetermined conversion 35 rate of the graft block-copolymer is lowered. A transitional temperature range of from -196 to 0°C is a distinctive feature of an embodiment of the regeneration of a dry powder of a used polytetrafluoroethylene. Starting with the 40 temperature of 0°C and further, the used polytetrafluoroethylene regeneration is performed in a manner similar to that described hereinbefore under suspension conditions (pressure of a monomer or of a mixture of 45 monomers, temperature, the presence of a liquid phase of the suspension—water or a corresponding liquid monomer and the like).
- In the process of the present invention a pure 50 and modified regeneration of a used polytetrafluoroethylene should be advantageously performed with the use of a periodic activation, whereby the required total dose is reduced due to a post-effect during the interval between two irradiation exposures.
- Practically all the above-described regenera-
- tion embodiments are characterized by a high thermal effect of the reaction. Temperature inside a reactor in case of a continuous and vigorous stirring of the suspension may be controlled by heat removal from the reactor walls by means of a heat-transfer medium (cooling agent) such as by means of water of a liquor supplied into a cooling jacket of the reactor. Fluorinated monomers employed for 55 regeneration of a used polytetrafluoroethylene, prior to being supplied into the reactor, are purified from inhibitors by conventional techniques such as by passing through an active charcoal.
- The microstructure of the regenerate powder particles is characterized by the presence of an inactive core—"nucleus" and an active layer—"coat" of a grafted fresh fluorinated polymer or copolymer ensuring a restoration and modification of the starting used polytetrafluoroethylene properties.
- During a heat-treatment-plastification of 60 blanks of regenerates produced by the process of the present invention, a matrix is formed from a fluoropolymer or fluorocopolymer which accepts, as a whole along with "nuclei" dispersed therewithin, all the stresses resulting from plastification without breaking the bonds formed between "nuclei" and "coat".
- Modified regenerates comprise grafted 65 block-copolymers based on a used polytetrafluoroethylene and fluoropolymers or fluorocopolymers with properties nearing those of the former which fluoropolymers or fluorocopolymers form a sufficiently thick layer around the "nucleus", which layer, unlike polytetrafluoroethylene, features a viscous fluidity. This automatically eliminates known technological difficulties encountered in the polytetrafluoroethylene processing. On the other hand, modified regenerates produced by the process of the present invention are superior over pure regenerates of copolymers, 70 since they include 50-90% of polytetrafluoroethylene.
- At the same time, the presence of a chemical bond between "coat" and "nucleus" as well 75 reduced coherence of a superficial layer of the used polytetrafluoroethylene particles during the graft block copolymerization impart to the regenerate certain advantages over corresponding mechanical mixtures of polymers.
- Production of modified regenerates is 80 profitable not only due to availability of a cheap raw material, viz. used polytetrafluoroethylene, but also due to a comparatively small consumption rate of expensive fluorinated monomers which are employed per se or, more often, in mixtures with cheaper tetrafluoroethylene and other reactive fluoromonomers. Modified regenerates are thermoplastic and may 85 be processed by methods traditionally employed for processing of thermoplastics such as extrusion, injection moulding, compression moulding at elevated temperatures and the like.

Modified regenerates may be used both individually and in composite materials.

For better understanding the process of the present invention is further illustrated in the following specific examples.

*Example 1*

Into a 2.5 l metallic sealed reactor provided with a stirrer (750 rpm) and cooling jacket, 50 g of a finely divided powder of a used polytetrafluoroethylene with a mean particle size of  $20\mu$  were charged along with 1.5l of twice distilled water. The reactor was pressurized by means of nitrogen to a pressure of 10 atm and then set to vacuum to a residual pressure of  $1 \times 10^{-2}$  mm Hg and twice purged with tetrafluoroethylene under 0.5 atm pressure followed by application of vacuum. Tetrafluoroethylene was then admitted into the system thus freed from oxygen. The oxygen content in the tetrafluoroethylene did not exceed 0.001% by volume. Activation of the graft block-copolymerization reaction was effected by irradiating the reactor with gamma-rays from  $\text{Co}^{60}$  at a dosage rate of  $1 \times 10^{-2}$  Rad/sec. The reaction was conducted for 20 hours. The total irradiation dose was 720 Rad. The temperature inside the reactor was maintained at  $70^\circ\text{C}$ . As the tetrafluoroethylene was consumed and pressure reduced to 4 atm, additional portions of the monomer, viz. tetrafluoroethylene, were fed into the reactor to the pressure of 5 atm. Added weight of the graft block copolymer washed with water and dried at  $150^\circ\text{C}$  was 8.1 g. From the powder of the resulting dried and finely divided regenerate a plate of 130x100x2mm size was made by compression moulding under the specific pressure of 500 kg/cm<sup>2</sup>. The resulting compressed blank was sintered in a free state at the temperature of  $370^\circ\text{C}$  during 2 hours, whereafter the plate was hardened by dipping into water at room temperature. Tests of the hardened plate showed the following characteristics:  $\rho=2.18 \text{ g/cm}^3$ ;  $\delta=240 \text{ kg/cm}^2$ ;  $\epsilon=220\%$ .

*Example 2*

Charged into a reactor were 100 g of a used polytetrafluoroethylene powder with a mean particle size of  $30\mu$ . The reaction preparation to the regeneration was effected in a manner similar to that described in Example 1. Tetrafluoroethylene pressure was 2 atm. Dose rate of gamma-radiation from  $\text{Co}^{60}$  was 0.17 Rad/sec. The temperature in the reactor was maintained at  $70^\circ\text{C}$ . Additional portions of tetrafluoroethylene were fed into the reactor under a reduced pressure down to 1 atm. Regeneration of the used polytetrafluoroethylene was conducted for 4 hours, the irradiation being interrupted after each 30 minutes. Total irradiation time was 3 hours. Added weight of the block copolymer was 52 g.

In a control test conducted in a manner similar to that described hereinabove but without the used polytetrafluoroethylene powder there was obtained 1.2 g of tetrafluoro-

ethylene homopolymer.

From the resulting regenerate a plate of 130x100x2mm size was made by compression moulding under a specific pressure of 500 kg/cm<sup>2</sup>. The blank was sintered in a free state at the temperature of  $370^\circ\text{C}$  during 2 hours, whereafter the plate was hardened by dipping into water at room temperature. Tests of the hardened plate showed the following characteristics:  $\rho=2.18 \text{ g/cm}^3$ ;  $\delta=240 \text{ kg/cm}^2$ ;  $\epsilon=220\%$ .

*Example 3*

50 g of a used polytetrafluoroethylene powder with a mean particle size of  $18\mu$  were charged into a reactor. The reactor preparation to regeneration was effected in a manner similar to that described in Example 1. An aqueous suspension was stabilized with a mixture of perfluorocarboxylic acids with 3 to 5 carbon atoms in an amount of about 0.005% by weight. Tetrafluoroethylene pressure was maintained at about 3 atm. The dose rate of gamma-radiation from  $\text{Co}^{60}$  was 0.51 Rad/sec. Regeneration of the used polytetrafluoroethylene was effected with discontinuous activation for 3 hours with intervals after each 15 minutes. Total irradiation time was 2 hours; total dose—3.672 Rad. Added weight of the block copolymer was 20 g. A plate manufactured by sintering in a free state had the following characteristics:  $\rho=2.21 \text{ g/cm}^3$ ;  $\delta=200 \text{ kg/cm}^2$ ;  $\epsilon=210\%$ .

*Example 4*

Into a reactor there were charged 50 g of a used polytetrafluoroethylene with a mean particle size of  $30\mu$ . The reactor preparation to regeneration of the used polytetrafluoroethylene was performed in a manner similar to that described in Example 1. Pressure of tetrafluoroethylene was maintained at about 1 atm by means of a discontinuous supply of fresh portions of tetrafluoroethylene when pressure inside the reactor dropped to 0.1 atm. Activation of the graft block-copolymerization reaction was performed with discontinuous irradiation by gamma-radiation from  $\text{Co}^{60}$  (after each 4 minutes) at the dose rate of 10 Rad/sec for 1 hour. Total irradiation time was 16 min; total dose—9,600 Rad; added weight of the block copolymer was 15 g. From the resulting regenerate a test sample was manufactured in a manner similar to that described in Example 2. The sample had the following characteristics  $\rho=2.23 \text{ g/cm}^3$ ;  $\delta=190 \text{ kg/cm}^2$ ;  $\epsilon=180\%$ .

*Example 5*

50 g of a used polytetrafluoroethylene powder with a mean particle size of  $20\mu$  were placed into a metallic reactor. The reactor was deaerated and twice purged with tetrafluoroethylene under a 0.5 atm pressure. Thereafter, the reactor was set under vacuum to a residual pressure of tetrafluoroethylene of  $1 \times 10^{-2}$  mm Hg. Then the reactor with the powder was cooled by liquid nitrogen to

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- 196°C. At this temperature the used polytetrafluoroethylene powder was irradiated by accelerated electrons at a dose rate of 100 Rad/sec during 1,000 sec. The total dose was 1.10<sup>5</sup> sec. On completion of the activation 15 g of tetrafluorotethylene were fed into the reactor at the temperature of -196°C. Then the temperature in the reactor was elevated to 0°C and 0.5 l of twice distilled water was poured thereinto. Then the temperature inside the reactor was elevated further to 70°C with vigorous stirring and the graft block copolymerization was completed at this temperature. Added weight of the grafted block copolymer was 12.2 g. A sample of the regenerate prepared as in Example 2 had the following characteristics:  $\rho=2.24 \text{ g/cm}^3$ ;  $\delta=170 \text{ kg/cm}^2$ ;  $\epsilon=160\%$ .
- Example 6*
- 50 g of the used polytetrafluoroethylene powder of particle size mentioned in Example 5 were cooled to -196°C and subjected to a plasma treatment in an atmosphere of helium under a 5 mm Hg pressure for 8 minutes; the treatment was effected using a high-frequency discharge. As a result of the plasma treatment the concentration of free radicals at the powder surface of the used PTFE was  $1.2 \times 10^{18}$  radicals/g thus corresponding to a total dose of about  $5 \times 10^5$  Rad. The powder had acquired a brown colour. After plasma treatment the powder was placed into a reactor into which 15 g of tetrafluoroethylene were charged at -196°C. Regeneration of the used polytetrafluoroethylene powder was further performed in a manner similar to that described in Example 5. Added weight was 14.5 g and the regenerate had a light-brown colour. A sample of the regenerate had the following characteristics:  $\rho=22.25 \text{ g/cm}^3$ ;  $\delta=160 \text{ kg/cm}^2$ ;  $\epsilon=130\%$ . Taking into account the regenerate colour, it should be preferably used in compositions with graphite, coke and other coloured fillers.
- Example 7*
- 50 g of a used polytetrafluoroethylene powder with a mean particle size of 45μ and maximal size of 100μ were placed into a reactor which was prepared for the reaction of graft block-copolymerization in a manner similar to that described in Example 1. Into the reactor was fed trifluorochloroethylene to the pressure of 3 atm. Activation was performed by means of gamma-radiation from Co<sup>60</sup> at the dose rate of 0.5 Rad/sec. The reaction temperature was 35°C, duration ~6 hours. The total dose was 10,800 Rad. Added weight of the grafted block copolymer in the modified regenerate of the used polytetrafluoroethylene was 10 g. From the regenerate a plate was manufactured of a 130x100x20 mm size which was sintered in a closed mould under conditions used in the processing of polytrifluorochloroethylene. The test results were as follows:  $\rho=2.30 \text{ g/cm}^3$ ;  $\delta=160 \text{ kg/cm}^2$ ;  $\epsilon=200\%$ .

*Example 8*

50 g of a used polytetrafluoroethylene powder with a mean particle size of 60μ were charged into a reactor. The reactor preparation for regeneration of the used polytetrafluoroethylene was effected as in Example 1. As the liquid phase use was made of trifluorochloroethylene condensed at -20°C under 1 atm pressure. Activation of the reaction of graft block copolymerization was performed by means of gamma-radiation from Co<sup>60</sup> with a dose rate of 0.3 Rad/sec for 4 hours. The total dose was 4,320 Rad. Added weight of the grafted block copolymer in the modified regenerate was 12 g. A sample made from the regenerate by extrusion had the following characteristics:  $\rho=2.25 \text{ g/cm}^3$ ;  $\delta=180 \text{ kg/cm}^2$ ;  $\epsilon=250\%$ .

*Example 9*

From a composition containing polytetrafluoroethylene and 20% by weight of coke 50 g of a powder were prepared with a mean particle size of 30μ. The reactor preparation for regeneration of the powder of polytetrafluoroethylene composition with coke was performed in a manner described in Example 1. In the reactor a pressure of tetrafluoroethylene of 2 atm was created and activation of the graft block copolymerization reaction was performed by means of gamma-radiation from Co<sup>60</sup> at a dose rate of 5 Rad/sec for 4 hours. Added weight of the grafted block copolymer was 22%; the regenerate was of a gray colour. Solid tablets of the regenerate prepared by sintering in a free state had the specific density  $\rho=2.24 \text{ g/cm}^3$ .

*Example 10*

50 g of a used polytetrafluoroethylene powder with a mean particle size of 30μ were charged into a reactor which was then charged with 1l of twice distilled water. The reactor with the charged material was pressurized by means of nitrogen under a pressure of 15 atm, then set under vacuum and twice purged with tetrafluoroethylene. Thereafter, the reactor was charged with a mixture of hexafluoropropylene and tetrafluoroethylene to a pressure of 10 atm, the partial pressure of hexafluoropropylene being 9 atm and that of tetrafluoroethylene - 1 atm.

The temperature in the reactor was maintained at 70°C. The reaction of modified regeneration of the used polytetrafluoroethylene was activated by means of gamma-radiation from Co<sup>60</sup> at a dose rate of 1 Rad/sec. As the monomers were consumed (mainly tetrafluoroethylene) the reactor was additionally supplied with tetrafluoroethylene to the initial pressure. The process was conducted for 10 hours. The total dose was 36,000 Rad. Added weight of the graft block copolymer in the modified regenerate was 10 g. Grafted layer consisted of 92% by weight of tetrafluoroethylene and 8% by weight of hexafluoropropylene. The modified regenerate was

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processed into solid samples by injection moulding and hot-compression moulding.

*Example 11*

- 5 An aqueous suspension of 50 g of a used polytetrafluoroethylene powder with a mean particle size of  $40\mu$  was placed into a reactor which was prepared for regeneration of the used polytetrafluoroethylene in a manner similar to that described in Example 1. In the  
 10 reactor a pressure of vinylidene fluoride of 15 atm was created. Activation of the graft block copolymerization reaction was performed by means of gamma-radiation from  $\text{Co}^{60}$  for 5 hours at a dose rate of 3 Rad/sec at the temperature of  $60^\circ\text{C}$ . The total dose was 54,000 Rad; added weight of the grafted block copolymer was 12 g. The modified regenerate was processed into a solid blank at the temperature of  $340^\circ\text{C}$ .
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*Example 12*

- An aqueous suspension of 50 g of a used polytetrafluoroethylene powder with a mean particle size of  $30\mu$  was charged into a reactor which was prepared for regeneration of the used polytetrafluoroethylene in a manner similar to that described in Example 1. Fed into the reactor was vinyl fluoride to a pressure of 30 atm. Activation of the graft block-copolymerization reaction was performed by means of gamma-radiation from  $\text{Co}^{60}$  for 5 hours at a dose rate of 5 Rad/sec at  $100^\circ\text{C}$  temperature. The total dose was 90,000 Rad. Added weight of the grafted block copolymer was 10.3 g. The modified regenerate was processed into a solid blank by hot-compression moulding.
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*Example 13*

- Under the conditions of Example 1, as the fluorinated monomer use was made of a mixture of tetrafluoroethylene and ethylene under a pressure of 50 atm. Partial pressure of tetrafluoroethylene was 2 atm, while that of ethylene was 48 atm. Dose rate of gamma-radiation from  $\text{Co}^{60}$  was 15 Rad/sec; temperature— $100^\circ\text{C}$ ; total duration of the reaction—10 hours. The total dose was 540,000 Rad. Added weight of the grafted block copolymer was 8.7 g. The modified regenerate was processed into a solid blank by hot-compression moulding.
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*Example 14*

- Under the conditions of Example 13, for regeneration of a used polytetrafluoroethylene powder in the form of a suspension use was made of a mixture of vinylidene fluoride with a partial pressure of 10 atm and ethylene with a partial pressure of 40 atm. Dose rate of gamma-radiation from  $\text{Co}^{60}$  was 20 Rad/sec; total duration of the reaction—14 hours. The total dose was 1,008,800 Rad; added weight of the grafted block copolymer was 13.3 g. The thus-modified regenerate was processed into a solid article by injection moulding at an elevated temperature under conditions usually employed for the processing of vinylidene
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fluoride-ethylene copolymers.

*Example 15*

Under the conditions of Example 1, for regeneration of a suspension of a used polytetrafluoroethylene powder use was made of a mixture of trifluorochloroethylene with a partial pressure of 1 atm and hexafluoropropylene with a partial pressure of 9 atm. Total pressure inside the reactor was 10 atm. Dose rate of gamma-radiation from  $\text{Co}^{60}$  was 1 Rad/sec, duration of the reaction was 10 hours; temperature  $60^\circ\text{C}$ . The total dose was 36,000 Rad; added weight of the grafted block copolymer was 8.7 g. The modified regenerate was processed into a solid article by injection moulding.

*Example 16*

Under conditions similar to those described in Example 1 a suspension of 50 g of a used polytetrafluoroethylene powder with a mean particle size of  $30\mu$  was subjected to regeneration in one litre of perfluorostyrene. Tetrafluoroethylene pressure inside the reactor was 5 atm; temperature  $30^\circ\text{C}$ , dose rate of gamma-radiation from  $\text{Co}^{60}$  was 0.2 Rad/sec. Duration of the reaction was 8 hours; the total dose 5,760 Rad; added weight of the grafted block copolymer was 7 g. The modified regenerate was processed into a solid article by extrusion.

WHAT WE CLAIM IS:—

1. A process for reprocessing used polytetrafluoroethylene comprising providing said used polytetrafluoroethylene in the form of a powder composed of discrete particles of size not greater than  $100\mu$ , irradiating said powder with ionising radiation to activate the polytetrafluoroethylene and contacting the activated polytetrafluoroethylene with a fluorinated monomer of formula  $\text{C}_2\text{F}_x\text{R}_{4-x}$  in which x is an integer from 1 to 4, R is hydrogen, a trifluoromethyl group, a chlorine atom a phenyl group or a pentafluorophenyl group, thereby effecting co-polymerisation of the polytetrafluoroethylene with the said monomer.

2. A process according to claim 1, wherein the ionizing radiation is gamma-radiation, X-rays, beta-radiation or accelerated electrons.

3. A process according to any preceding claim, in which the polytetrafluoroethylene powder is suspended in water or the fluorinated monomer defined in claim 1 and is irradiated in the suspended state.

4. A process according to any preceding claim, in which the activation is carried out under an atmosphere containing not more than  $2 \times 10^{-3}$  vol % of oxygen, said atmosphere being provided by carrying out the activation (a) under a reduced pressure of inert gas or fluorinated monomer vapour not lower than 5 mm Hg, or, (b) under reduced pressure not exceeding  $1 \times 10^{-2}$  mm Hg, or (c) under pressure of the vapour of said monomer of from 0.1 to 50 atmospheres.

5. A process according to any preceding

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claim, in which the activation comprises irradiation of total dose  $10^3$  to  $10^6$  Rad at a dose rate of from  $10^{-2}$  to  $10^2$  Rad/sec.

6. A process according to any preceding claim, carried out at a temperature of from  $-196$  to  $+100^\circ\text{C}$ .

7. A process according to any preceding claim, wherein the fluorinated monomer is tetrafluoroethylene; the copolymerisation is performed in an aqueous suspension of the used polytetrafluoroethylene powder having a mean particle size of not greater than  $30\mu$ ; activation of said suspension is effected in an atmosphere of tetrafluoroethylene with a total dose of from  $1 \times 10^3$  to  $1 \times 10^4$  Rad at a dose rate of from  $1 \times 10^{-2}$  to  $10$  Rad/sec, at a temperature of  $+70^\circ\text{C}$  and under a tetrafluoroethylene atmosphere of pressure of from 0.1 to 5 atm.

8. A process according to any one of claims 1 to 6, wherein the fluorinated monomer is a compound of the formula  $\text{C}_2\text{F}_x\text{R}_{4-x}$  where  $x$  is 1, 2 or 3, R is hydrogen, or where  $x$  is 3 and R is chlorine, the polytetrafluoroethylene is activated in suspension under an atmosphere of at least one of said fluorinated monomers, with a total dose of from  $1 \times 10^3$  to  $1 \times 10^5$  Rad at a dose rate of from  $1 \times 10^{-1}$  to  $50$  Rad/sec and at a temperature of from  $-20$  to  $+100^\circ\text{C}$ .

9. A process according to any one of claims 1 to 6, wherein the monomer is a mixture of (a) a fluorinated monomer of the formula:  $\text{C}_2\text{F}_x\text{R}_{4-x}$  where  $x$  is an integer from 1 to 4 and R is hydrogen or x is 3 and R is a chlorine atom with (b) ethylene, vinyl chloride, or a compound of the formula  $\text{C}_2\text{F}_x\text{R}_{4-x}$  where  $x$  is 3 and R is  $\text{CF}_3$ ,  $\text{C}_6\text{F}_5$  or  $\text{C}_6\text{H}_5$ ; the used polytetrafluoroethylene is activated in suspension under an atmosphere of said mixture of the monomers with a total dose of from

$1 \times 10^4$  to  $1 \times 10^6$  Rad, at a dose rate of from 1 to  $1 \times 10^2$  Rad/sec, at a temperature within the range of from  $30$  to  $100^\circ\text{C}$  and under a pressure of said mixture of the monomers of from 1 to 50 atm.

10. A process according to any one of claims 1 to 6, in which used polytetrafluoroethylene powder is activated at a temperature of from  $-196$  to  $-130^\circ\text{C}$  under reduced pressure of not more than  $1 \times 10^{-2}$  mm Hg, thereafter one of fluorinated monomers of the formula  $\text{C}_2\text{F}_x\text{R}_{4-x}$  where x is an integer from 1 to 4, R is hydrogan or x is 3 and R is chlorine is added, the temperature is raised to  $0^\circ\text{C}$ ; water is added to form an aqueous suspension of the activated polytetrafluoroethylene and the graft block-copolymerization is completed at a temperature of from 0 to  $100^\circ\text{C}$ .

11. A process according to any one of claims 1, 2, 4, 5 and 6, wherein the used polytetrafluoroethylene is in the form of a dry powder and activation is effected by means of a plasma treatment.

12. A process for regenerating used polytetrafluoroethylene substantially as described in the specification and Examples 1 to 16 set forth hereinbefore.

13. Block-copolymers based on used polytetrafluoroethylene whenever produced by the process claimed in any one of the claims 1 to 12.

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